

Chemical interactions during the electrospinning of binary microfibers of plasma polyaniline and polyethylene oxide

R. Ramírez^{1,2}, J.C. Palacios², M.G. Olayo¹, F.G. Flores^{1,2}, E. Colín², M. González-Torres^{1,5}, L.M. Gómez⁴, R. Valdivia³, M.R. Mejía, E.A. González, G.J. Cruz^{1*}.

¹Departamento de Física, ³Departamento de Medio Ambiente, Instituto Nacional de Investigaciones Nucleares. Carretera México-Toluca s/n, La Marquesa, Ocoyoacac, EdMx., CP 52750, México.

²Facultad de Ingeniería, Universidad Autónoma del Estado de México. Cerro de Coatepec, Paseo Universidad s/n, Universitaria, 50130 Toluca de Lerdo, EdMx.

⁴División de Estudios de Posgrado e Investigación, Tecnológico Nacional de México / Instituto Tecnológico de Toluca, Av. Tecnológico S/N, Col. Agrícola Bellavista, Metepec, EdMx, CP 52149, México

⁵División de Ingeniería Industrial, Tecnológico de Estudios Superiores de Tianguistenco. Carretera Tenango-La Marquesa km. 22, Tianguistenco, Estado de México.

*guillermo.cruz@inin.gob.mx

Abstract:

Electrospun microfibers of semisoluble polyaniline (PAn) synthesized by plasma combined with polyethylene oxide (PEO) were formed to conjugate the properties of both polymers in potential biomaterials. The average fiber diameter was between 1.07 and 1.25 μm with chemical groups and electromagnetic absorption in the UV-Vis interval that suggest chemical modification of both polymers during the electrospinning. The electromagnetic absorption of the fibers was higher in the UV zone than those of their individual components which can be due to the voids among fibers on the surface.

Keywords: plasma, polyaniline, polyethylene oxide, fibers.

1. Introduction

The chemical structure of polyaniline (PAn) synthesized by plasma is formed by crosslinked networks of anilines that results insoluble or semisoluble in many solvents [1,2]. Insoluble polymers cannot form electro-spun fibers, since high solubility is required; however, semisoluble polymers can be spun combining them with another highly soluble material, such as polyethylene oxide (PEO) [3,4]. This kind of binary fibers could be used as an artificial matrix for cell adhesion and proliferation. Therefore, the aim of this work was the synthesis of micro electro-spun fibers composed of semisoluble plasma PAn and PEO.

2. Methodology

Semisoluble PAn was synthesized in a tubular glass reactor with glow discharges at 20 and 40 W at 13.56 MHz with resistive coupling. The PAn-PEO fibers were made in three steps: 1) 0.25 g of PAn was dissolved in 1 mL of acetone; 2) 0.5 g of PEO was dissolved in 10 mL of chloroform; 3) both solutions were mixed to form binary PAn-PEO mixtures with PEO/PAn=2 mass ratio that were processed in a home-made electrospinning equipment with the following conditions: distance between electrodes of 12 cm, roller speed of 2500 rpm, injection speed of 0.6 mL/h, diameter of the injection needle of 0.15 mm and potential of 12.2 kV.

The morphological analysis was carried out in a Jeol IT-100 scanning electron microscope. The fiber diameter was processed with the Olympus Measure IT program. The structural analysis was performed with a Thermo Scientific iD5 infrared spectrometer in ATR mode. The electromagnetic fiber absorption was analyzed by UV-Vis spectroscopy in a Thermo Scientific Evolution 600 spectrophotometer.

3. Results

3.1 Morphological Analysis

Figure 1 shows 2 micrographs of PAn-PEO electro-spun fibers with PAn synthesized at 20 and 40 W. The fibers with PAn at 20 W, Fig. 1a, are compact with an average diameter of 1.25 μm oriented in the same direction with some fragments on the surface. The fibers with PAn at 40 W, Fig. 1b, are branched with different diameter, on average 1.07 μm , with greater dispersion and less orientation than in the previous case.

3.2 Structural analysis

Figure 2 shows infrared spectra of PEO, PAn and PAn-PEO fibers. The chemical groups of PEO are associated with C-C, C-H and C-O bonds in different wave numbers [5], see Fig. 2. PAn groups are associated with =C-H, N-H, C-N, C=C, $\approx\text{C}\approx$, $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ bonds of the resonant structures of combinations of aniline molecules [6,7]. The chemical groups of the fibers include most of both compounds; however, there are some that do not appear in the fibers, N-H bonds at 3366 cm^{-1} , $\text{C}\equiv\text{C}$ and/or $\text{C}\equiv\text{N}$ at 2212 cm^{-1} and C=C and/or C-N at 1600 cm^{-1} . The =C-H group at 686 cm^{-1} has a very small participation in the fibers. The PEO/PAn=2 mass ratio in the fibers suggests that the PAn absorptions are about half that of PEO but should not disappear.

The disappearance of specific absorptions suggests chemical modification of PAn and PEO promoted mainly by the intense electric fields in which the polymeric fluids are subjected in the path from one electrode to another during the electrospinning. The disappearance of N-H groups and the reduction of =C-H suggest dehydrogenation and the disappearance of $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$,

C=C and C-N suggest changes in the oxidation of PAN during the process.

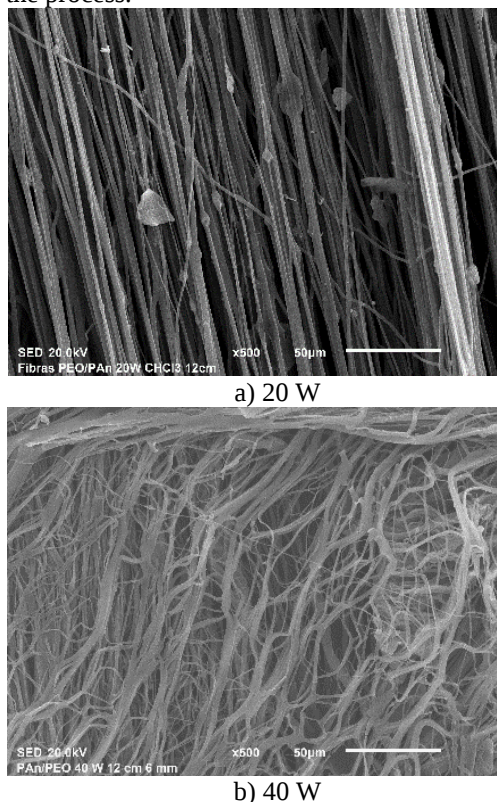


Figure 1. Fibers composed of PAN-PEO with PAN synthesized at 20 W and 40 W. Note how the fibers at 20 W are more compact and oriented in the same direction and that those at 40 W are more branched.

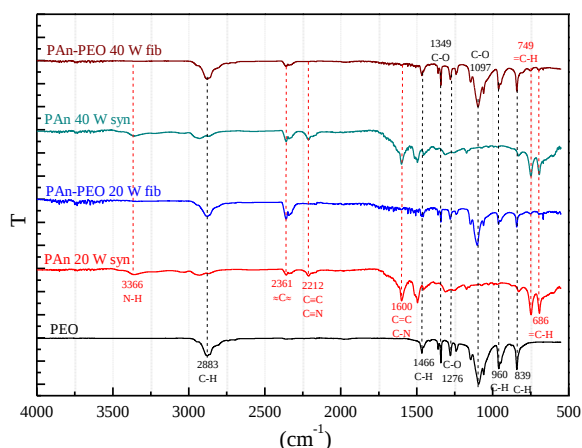


Figure 2. IR spectra of PAN, PEO and PAN/PEO fibers. The disappearance of the 1600 cm^{-1} absorption in the fibers suggest chemical modifications in PAN during the electrospinning.

3.3 Electromagnetic Absorption

The electromagnetic absorption of PEO, PAN and PAN-PEO fibers is presented in Figure 3. The lowest absorption was found in PEO and the highest in PAN-PEO

fibers with PAN synthesized at 20 W. It should be noted that both PAN-PEO fibers have greater absorption in the 200-400 nm range than their individual components. The fiber alignment on the surface may increase the electromagnetic absorption in this case.

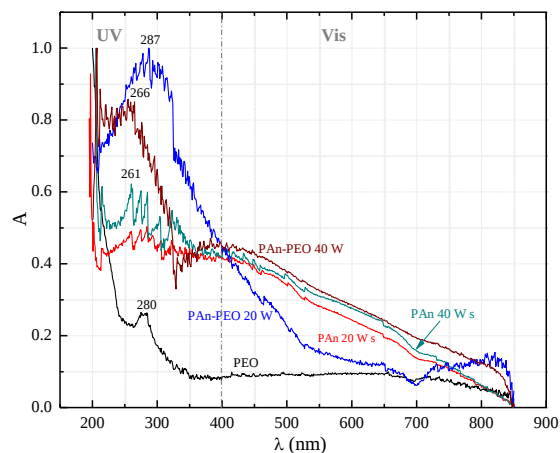


Figure 3. Electromagnetic absorption of PEO, PAN and PAN-PEO fibers. In the 200-400 nm interval the absorption of fibers is higher than that of PAN and PEO.

Conclusions

Binary solutions of PAN and PEO were prepared to electro spin them to form microfibers of both polymers. The fiber diameter was between 1.07 and 1.25 μm . The chemical groups in the fibers suggest chemical modification in the structure of the polymers during the electrospinning, mainly as dehydrogenation and oxidation. The binary fibers showed higher electromagnetic absorption in the 200-400 nm range than their individual components.

Acknowledgement

R. Ramírez and F.G. Flores acknowledge CONACyT for the master science scholarships received.

1. References

- [1] M.G. Olayo, MA. Enríquez, G.J. Cruz, J. Morales, R. Olayo, *Journal of Applied Polymer Science*, 102, 4682-4689 (2006).
- [2] C.I. Awuzie, *Materials Today: Proceedings*, 4 (4), 5721-5726 (2017).
- [3] L. Ma, L. Deng, J. Chen, *Drug Development and Industrial Pharmacy*, 40 (7), 845-851 (2013).
- [4] F. Hsiao, P.Y. Huang, T. Aoyagi, S.F. Chang, J. Liaw, *Journal of Food and Drug Analysis*, 26(2), 869-878 (2018).
- [5] M.A. Morsi, M. Abdelaziz, A.H. Oraby, I. Mokhles, *Journal of Physics and Chemistry of Solids*, 125, 103-114 (2019).
- [6] A.G. Yavuz, A. Uygur, V.R. Bhethanabotla, *Carbohydrate Polymers*, 75 (3), 448-453 (2009).
- [7] K.A. Ibrahim, *Arabian Journal of Chemistry*, 10(2), S2668 – S2674 (2017).